LAKE SUPERIOR WET DEPOSITION 1983

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INTRODUCTION

Nutrient and contaminant inputs from atmospheric sources have been a major concern for Great Lakes water quality management since the seventies. In 1977, the International Joint Commision (IJC) Upper Lakes Reference Group concluded that Lake Superior was particularly susceptible to air borne contaminants because of its geographical and physical characteristics. It is downwind from major industrial centres and direct precipitation on the lake surface accounts for over 50% of Lake Superior's annual input of water (Bennett 1978). It has a retention time of 177 years and a very low sedimentation rate of 0.1 to 2.0 mm per year (Kemp et al 1978) compared to 13.4 mm in Lake Erie. Substances entering the lake are likely to have a long retention time because there are few mechanisms to remove them from the water column. The need to obtain reliable atmospheric loading estimates was cited in the 1978 CAN/US Great Lakes Water Quality Agreement. As part of the IJC Great Lakes International Surveillance Plan (GLISP) 1983 Lake Superior Intensive Study Plan the Water Quality Branch of Environment Canada operated a network of four precipitation chemistry stations in the Lake Superior Basin. Two of these stations have been operating since 1980 while the other two were established in 1982. At each station, monthly wet-only precipitation samples were collected for chemical analyses. This report presents atmospheric loading estimates based on the results of that study.

SUMMARY AND CONCLUSIONS

Wet deposition estimates were computed from monthly wet precipitation samples from Lake Superior. Sulphate and Nitrogen loadings from wet precipitation corresponded to 152.6 and 40.2 thousand tonnes per year respectively. On a percentage basis, wet deposition of suphate was 22% of the total load whereas wet deposition of nitrogen was 55% of the total load. Atmospheric sources for the other major ions were less significant, ranging from 1-6% of the total load. Using a simple mass balance model, these atmospheric loading estimates are consistent with changes that have occurred in the lake chemistry relative to the conservative major ions. For more refined and reliable atmospheric loading estimates, long term records are necessary to provide information on the precision, variability and trends of atmospheric loadings.

FIELD SAMPLING

The sampling sites chosen were Sibley Provincial Park, Rossport, Wawa and Sault-Ste-Marie (fig. 1). With the exception of Sault-Ste-Marie, all the sampling stations are located on private property and operated by the property owners. The site at Sibley Provincial Park is located at Silver Inlet at the tip of the

pennisula. This station has been in operation since 1980. The Rossport station is on a private lot in Rossport about half a kilometer from the main highway. The station in Wawa is at the mouth of the Magpie river, about 10 Km from the town of Wawa. The sampling at Sault-Ste-Marie is situated at the Sault-Ste-Marie airport and serviced by the weather office at the airport. These sites have been chosen according to the criteria to be as close to the Lake as possible but free of any major obstacles and local emissions. However, logistical and practical constraints also influenced the choice of the sampling sites.

The precipitation collector is a Sangamo type A collector manufactured by M.I.C. of Toronto. Samples are collected in a polyethylene bucket which is covered by a movable lid during dry periods. The movement of the lid is activated by two electric sensor grids which detect precipitation. The sample is emptied into another polyethylene bottle and the bucket changed at the end of the calendar month, and the samples are mailed to Burlington for analysis. Methods of analyses are described in the Analytical Methods Manual (Department of the Environment, 1979).

RESULTS AND DISCUSSIONS

Table 1 summarizes the yearly mean measurements over the study period (Sibley and Sault-Ste-Marie had been in operation since 1980). To allow for the varying amount of precipitation from month to month, the volume weighted mean concentrations are shown

in Table 2. Average precipitation over the four year period was 57.7 cm per year. The long term average precipitation for the Basin is 72.5 cm per year.

Temporal Variation

Data from Sibley and Sault-Ste-Marie were fairly consistent over the four year period with the exception of pH at Sibley which showed a gradual decrease from 5.1 to 4.3. The decrease in pH also parallelled an decrease in calcium and magnesium concentrations. This was likely caused by a change in the sampling location within the Park. The sampler was moved from the interior of the Park to the edge of the Park at Silver Inlet in 1982. The former site was close to the Park's main gravel road which made the site less than ideal. Contamination from road dust could raise calcium and magnesium contents and the pH. pH data from Sault-Ste-Marie also showed a slight decrease, but the change was not considered significant. The short time period of this database really does not permit any meaningful interpretaion of trends or changes in the chemistry.

Spatial Variation

Over the study period, samples from Sault-Ste-Marie consisitently had higher ion concentrations than Sibley samples most notably in nitrate and sulphate, both of which are products of fuel emission. The differences between the Sault-Ste-Marie station and the other stations can be attributed to geographical or local

effects. Geographically Sibley Park is about 2 degrees or 130 Km northwest of Sault-Ste-Marie. The weather patterns and air masses affecting the two sites are likely to be different. Sault-Ste-Marie is downwind of the industrial states of Michigan and Wisconsin, whereas Sibley is downwind from the Prairies. Airmasses which travel across the industrial Mid-Western States, where nitrogen and sulphur emmissions are higher than the Prairies, results in higher nitrogen and sulphate deposition in Sault-Ste-Marie. Preliminary data from the Canadian Air and Precipitation Monitoring network (CAPMoN 1983) show that Ontario and Quebec have higher nitrate and sulphate concentrations in wet precipitaion than the rest of Canada. Locally although the sampler at Sault-Ste-Marie is located whithin the Airport compound, traffic at the airport is very light, and the airport is far away and upwind from the city, thus influence from local emmissions is probably minimal. In all likelihood, the higher nitrate and sulphate readings from Sault-Ste-Marie was a probable occurence. The limited size of this data provide very little information about the temporal or spatial distribution of precipitation chemistry basin.

LOADINGS

Loading calculations based on these four years of data are estimates only. The accuracies of these estimates depend on many factors such as sampling frequency, representativeness of sampling locations, spatial and temporal variations etc. In reality,

logistical and cost constraints also influence the overall sampling design.

For wet deposition, the following formula is used in computing the atmospheric loads to Lake Superior:

Annual loading = 12 (mos) X (ppt in mm/mos) X (VWM mg/L) X (Lake surface Km2)

where VWM = average volume weighted mean concentrations from the sampling stations

ppt = average monthly precipitation

Lake surface area = 82,236 Km2

Using a simple model of inputs and outputs with some simplifying assumptions it is possible to estimate the relative importance and the accuracy of these loading estimates. Loading estimates were computed using the formula described above for the various parameters measured and are tabulated in Table 3. Generally, annual loadings to the lake were fairly uniform from year to year. The notable exception was calcium which was substantiately lower in 1983. This was probably due to the change in sampling location at Sibley (noted above) and the addition of two rural stations in Wawa and Rossport. Because 1983 stations have a more even coverage of the Basin, 1983 loading figures will be used in the following discussion.

In 1983 sulphate had the highest load with 153 thousand tonnes

per year. This excessive input of atmospheric sulphate had been predicted by Thompson (1978) based on mass balance and electroneutrality calculations. Total nitrogen (sum of nitrate and kjeldahl nitrogen) showed the second highest with 40.2 thousand tonnes per year. Phosphorus was the least with only 462 tonnes per year, about 0.3% of the sulphate loading. A comparison of these figures with the 1977 IJC report shows that, with the exception of reactive silicates, the numbers are fairly comparable. The 1977 IJC figures were based on bulk (wet + dry) deposition data therefore they would expected to be higher.

The relative importance of atmospheric loading was demonstrated when these figures were examined in relation to total loadings to the Lake (Table 4). Assuming that dry deposition loadings to Lake Superior were relatively minor and internal loading to the lake was nil, the sum of wet deposition and loadings from tributaries, industries and municipalities would be representative of the total loading to the lake (Table 4). From these data it was evident that atmospheric inputs of nitrogen, sulphate and phosphorus constituted major proportions of the total inputs. Wet deposition of nitrogen contributed 54% of the total load, while for sulphate and phosphorus, constituted 22% and 13% respectively. For other major ions, atmospheric sources were much less significant ranging from 1-6% of the total load. Thus atmospheric deposition continued to be a major source of nutrients to Lake Superior.

In order to determine the relative accuracies of these loading figures, a simple mass balance model was used. In this model, material input to Lake Superior was assumed equal to the sum of wet deposition and tributaries, industrial and municipal loadings. Dry deposition and internal loadings were assumed to be negligible. Material output of Lake Superior was set equal to the ouflow via the St. Marys River; losses of material via sedimentation were considered insignificant. In the final mass balance equation, material input should be either greater or equal to output. The net amount of material retained by the Lake was then divided by the Lake volume (11,900 KM3) to arrive at an expected change in Lake concentration. The predicted rate of change was then compared with Lake data collected between 1973 and 1983. The results are summarized in Table 5.

Agreement between the concentration changes predicted by the model and the measured concentration changes was very good for dissolved major ions (SO4, Cl, Na, Ca Mg and K) but the fit was not as good for nitrate and phosphorus. For dissolved major ions, the predicted values and the actual measured values were within 0.1 mg/L of each other. However, for phosphorus, which was predicted to increase to .008 mg/L, showed a decrease in concentration to .003 mg/L, while Nitrate had an increase of 0.029 mg/L from 1973 to 1983 compared to a predicted increase of 0.001 mg/L.

The two underlying assumptions in the mass balance equation are that sedimentation is negligible and that all of the retained material in the lake is inert in the water column. Dissolved major ions readily meet these two criteria. Their concentrations are high enough to be considered biologically inert, and as they are very much below their saturation concentrations so they do not precipitate out. But the chemistries of nitrate and phosphorus in lake water are very different from the major ions. These elements are biologically active. They readily interconvert from soluble to particulate species and vice versa, and particulate species can be removed from the water column through sedimentation. The observed decrease in phosphorus concentration in Lake Superior has not been explained. For nitrate, according to the model calculation, the expected increase in nitrate was only a fraction of what was actually measured. Nitrate concentrations in Lake Huron (Stevens 1985) and the Lower Great Lakes have also been reported to be increasing (IJC 1983) at rates of .004 mg/L and .008 mg/L per year respectively. Total nitrogen, the sum of kjeldahl nitrogen and nitrate, might show a better indication of changes in nitrogen in Lake Superior. The calculated increase for total nitrogen is .0039 mg/l per year or an increase of .039 mg/L over a ten year period. The computed value for total nitrogen is 0.408 mg/L versus an observed value of 0.405 mg/L. Again, there were no major discrepencies between the predicted and the observed values.

Based on this simple mass balance model, it appears that atmospheric loading estimates are fairly consistent with changes that have occurred in the lake chemistry relative to the conservative major ions. This does not hold for the biologically active nutrient parameters such as nitrate and phosphorus. However, this is not unexpected since these nutrient parameters can undergo many transformations and thus be sedimented out of the system.

These estimates are based on a single year of sampling and a small number of sampling sites. Atmospheric deposition as is rainfall itself is subject to large and rapid fluctuations in space and time. For more refined and reliable atmospheric loading estimates, long term records are necessary to provide information on the precision, variability and trends of atmospheric loadings.

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TABLE 1 ANNUAL MEAN CONCENTRAIONS IN LAKE SUPERIOR WET PRECIPITATION (mg/L)

	1983					1982			1981			1980		
PARAMETER	SB	RP	WW	SM	I	SB	SM	I	SB	SM	I	SB	SM	I
VOL	1673	1615	1704	1539	1633	1861	1868	1864	1263	1417	1340	1294	1146	1218
pH	4.4	4.3	4.1	4.6	4.3	4.3	4.7	4.5	5.0	4.7	4.8	4.8	5.5	5.1
COND	18.3	28.3	29.2	32.1	27.0	22.3	29.3	25.9	27.4	37.6	32.5	15.3	35.9	25.6
T.P.	0.013	0.013	0.007	0.008	0.010	0.008	0.006	0.007	0.013	0.006	0.100	0.007	0.008	0.008
NO3	0.258	0.448	0.439	0.527	0.418	0.332	0.498	0.415	0.428	0.583	0.505	0.309	0.735	0.522
TKN	0.300	0.656	0.423	0.424	0.451	0.451	0.479	0.465	0.594	0.417	0.505	0.319	0.522	0.435
NH3	0.197	0.467	0.319	0.327	0.327	0.341	0.387	0.364	0.409	0.336	0.372	0.204	0.431	0.317
SiO2	0.042	0.049	0.068	0.071	0.057	0.028	0.072	0.050	0.056	0.075	0.066	0.042	0.117	0.079
Na	0.059	0.246	0.128	0.088	0.130	0.075	0.084	0.079	0.130	0.105	0.117	0.140	0.278	0.209
Ca	0.315	0.463	0.526	0.988	0.573	0.319	2.770	1.540	0.976	1.680	1.328	0.539	2.990	1.764
Mg	0.065	0.058	0.062	0.174	0.089	0.055	0.127	0.091	0.261	0.119	0.19	0.096	0.291	0.193
K	0.075	0.155	0.048	0.048	0.081	0.088	0.044	0.066	0.144	0.060	0.102	0.089	0.100	0.094
Cl	0.190	0.459	0.324	0.282	0.313	0.213	0.326	0.269	0.871	0.494	0.682	0.366	0.725	0.545
SO4	1.858	3.353	3.454	3.847	3.128	2.358	3.622	2.990	2.743	3.621	3.182	1.456	4.974	3.215

SB = Sibley
RP = Rossport
WW = Wawa
SM = Sault-Ste-Marie
I = basin mean

TABLE 2 VOLUME WEIGHTED MEAN CONCENTRATIONS IN LAKE SUPERIOR WET PRECIPITATION (MG/L)

	1983					1982			1981			1980		
PARAMETER	SB	RP	NW	SM	X	SB	SM	X	SB	SM	X	SB	SM	X
PPT	53.3	51.4	54.3	49.0	52.0	59.3	59.5	59.4	40.2	45.1	42.6	41.2	36.4	38.8
T.P.	0.012	0.011	0.008	0.006	0.009	0.008	0.006	0.007	0.012	0.005	0.008	0.007	0.008	0.008
NO3	0.229	0.433	0.367	0.444	0.368	0.256	0.445	0.350	0.482	0.467	0.474	0.313	0.712	0.512
TKN	0.269	0.603	0.438	0.352	0.415	0.352	0.432	0.392	0.639	0.391	0.515	0.307	0.559	0.433
NH3	0.176	0.426	0.333	0.285	0.305	0.257	0.343	0.300	0.468	0.308	0.388	0.203	0.452	0.327
SiO2	0.044	0.047	0.052	0.071	0.053	0.025	0.061	0.044	0.062	0.063	0.062	0.028	0.105	0.066
Na	0.052	0.249	0.103	0.072	0.120	0.056	0.081	0.068	0.133	0.086	0.109	0.130	0.169	0.149
Ca	0.311	0.410	0.465	0.955	0.535	0.285	1.933	1.109	1.015	1.138	1.076	0.505	2.334	1.434
Mg	0.063	0.053	0.057	0.161	0.083	0.049	0.104	0.076	0.262	0.088	0.175	0.088	0.262	0.175
K	0.076	0.189	0.044	0.045	0.088	0.084	0.041	0.062	0.162	0.055	0.108	0.076	0.091	0.084
Cl	0.172	0.440	0.251	0.260	0.281	0.155	0.258	0.206	0.922	0.410	0.666	0.398	0.484	0.441
SO4	1.688	3.135	3.162	3.632	2.974	1.895	3.240	2.567	3.276	3.480	3.378	1.430	5.003	3.216

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PPT	53.3	51.4	54.3	49.0	52.0	59.3	59.5	59.4	40.2	45.1	42.6	41.2	36.4	38.8
T.P.	0.120	0.011	0.008	0.008	0.009	0.008	0.006	0.007	0.012	0.005	0.008	0.007	0.008	0.008
NO3	0.229	0.433	0.367	0.444	0.368	0.256	0.445	0.350	0.482	0.467	0.474	0.313	0.712	0.512
TKN	0.269	0.603	0.438	0.352	0.415	0.352	0.432	0.392	0.639	0.391	0.515	0.307	0.559	0.433
NH3	0.176	0.426	0.333	0.285	0.305	0.257	0.343	0.300	0.468	0.308	0.388	0.203	0.452	0.327
SiO2	0.044	0.047	0.052	0.071	0.053	0.025	0.061	0.044	0.062	0.063	0.062	0.028	0.105	0.066
Na	0.052	0.249	0.103	0.078	0.120	0.056	0.081	0.068	0.133	0.086	0.109	0.130	0.169	0.149
Ca	0.311	0.410	0.465	0.955	0.535	0.285	1.933	1.109	1.015	1.138	1.076	0.505	2.334	1.434
Mg	0.063	0.053	0.057	0.161	0.083	0.049	0.104	0.076	0.262	0.088	0.175	0.088	0.262	0.175
K	0.076	0.189	0.044	0.045	0.088	0.084	0.041	0.062	0.162	0.055	0.108	0.078	0.091	0.084
Cl	0.172	0.440	0.251	0.260	0.281	0.155	0.258	0.206	0.922	0.410	0.666	0.398	0.484	0.441
SO4	1.688	3.135	3.162	3.632	2.974	1.895	3.240	2.567	3.276	3.480	3.378	1.430	5.003	3.216

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TABLE 3. LAKE SUPERIOR ATMOSPHERIC WET-LOADING (X 1000 TONNES/YR)

PARAMETER	1983	1982	1981	1980	1980-83	1977
T.P.	0.46	0.41	0.34	0.31	0.37	0.80
NO3	18.88	20.51	19.93	19.60	19.73	ND
TKN	21.29	22.98	21.65	16.58	20.62	ND
NH3	15.65	17.58	16.31	12.52	15.52	ND
T.N.	40.17	43.49	41.78	36.18	40.35	56.00
SiO2	2.72	2.58	2.61	2.53	2.61	26.00
Na	6.16	3.98	4.58	5.71	5.11	15.00
Ca	27.45	65.01	45.23	54.91	48.15	33.00
Mg	4.26	4.46	7.36	6.70	5.69	5.60
K	4.54	3.64	4.54	3.21	3.98	13.00
Cl	14.42	12.07	28.00	16.88	17.84	55.00
SO4	152.61	150.47	142.00	123.14	142.06	ND

ND = no data

TABLE 4

	CONC IN MG/L		LOADING X 1000 TONNE/YR				
PARAMETER	WET PRECIP.	LAKE	WET DEPOSITION	TRIB.	IND & MUNICIPAL	TOTAL	% WET/TOT
T.P.	0.01	0.003	0.46	2.83	0.231	3.52	13.07
NO3	0.418	0.321	18.88	6.79	0.08	25.75	73.32
TKN	0.452	0.084	21.29	25.91	0.69	47.89	44.46
T.N.	0.869	0.405	40.18	33.70	1.06	73.93	54.35
SiO2	0.057	2.32	2.72	412.57	10.25	425.54	0.64
Na	0.13	1.30	6.16	196.00	31.57	233.72	2.64
Ca	0.573	13.35	27.45	1193.55	15.62	1236.62	2.22
Mg	0.089	2.74	4.26	361.35	3.36	368.97	1.15
K	0.081	0.50	4.52	86.14	3.00	93.66	4.83
Cl	0.313	1.32	14.42	212.06	32.56	259.04	5.57
SO4	3.128	3.44	152.61	512.95	22.30	687.86	22.19

TABLE 5

PARAMETER	INPUT X 1000 TONNE/YR	OUTFLOW X 1000 TONNE/YR	AMOUNT RETAINED TONNE/YR	INCREASE IN CONC mg/L/YR	1973 LAKE DATA mg/L	EXPECTED 1983 CONC mg/L	OBSERVED 1983 CONC mg/L
T.P.	3.52	0.236	3.289	0.00027	0.0062	0.009	0.0035
TKN	47.89	5.65	42.240	0.0036	ND	ND	0.084
T.N.	73.93	27.27	46.660	0.0039	0.368	0.408	0.405
SiO2	425.54	156.24	269.300	0.023	2.418	2.640	2.320
Na	233.72	87.55	146.170	0.012	1.260	1.380	1.300
Ca	1236.62	899.05	337.570	0.028	12.920	13.200	13.350
Mg	368.97	184.52	184.450	0.016	2.660	2.810	2.740
K	93.66	33.67	59.190	0.005	0.480	0.530	0.500
Cl	259.04	88.89	170.150	0.143	1.180	1.320	1.320
SO4	687.86	231.66	456.200	0.038	3.010	3.390	3.440
NO3	25.75	21.62	4.130	0.0003	0.283	0.286	0.321

* ND= no data

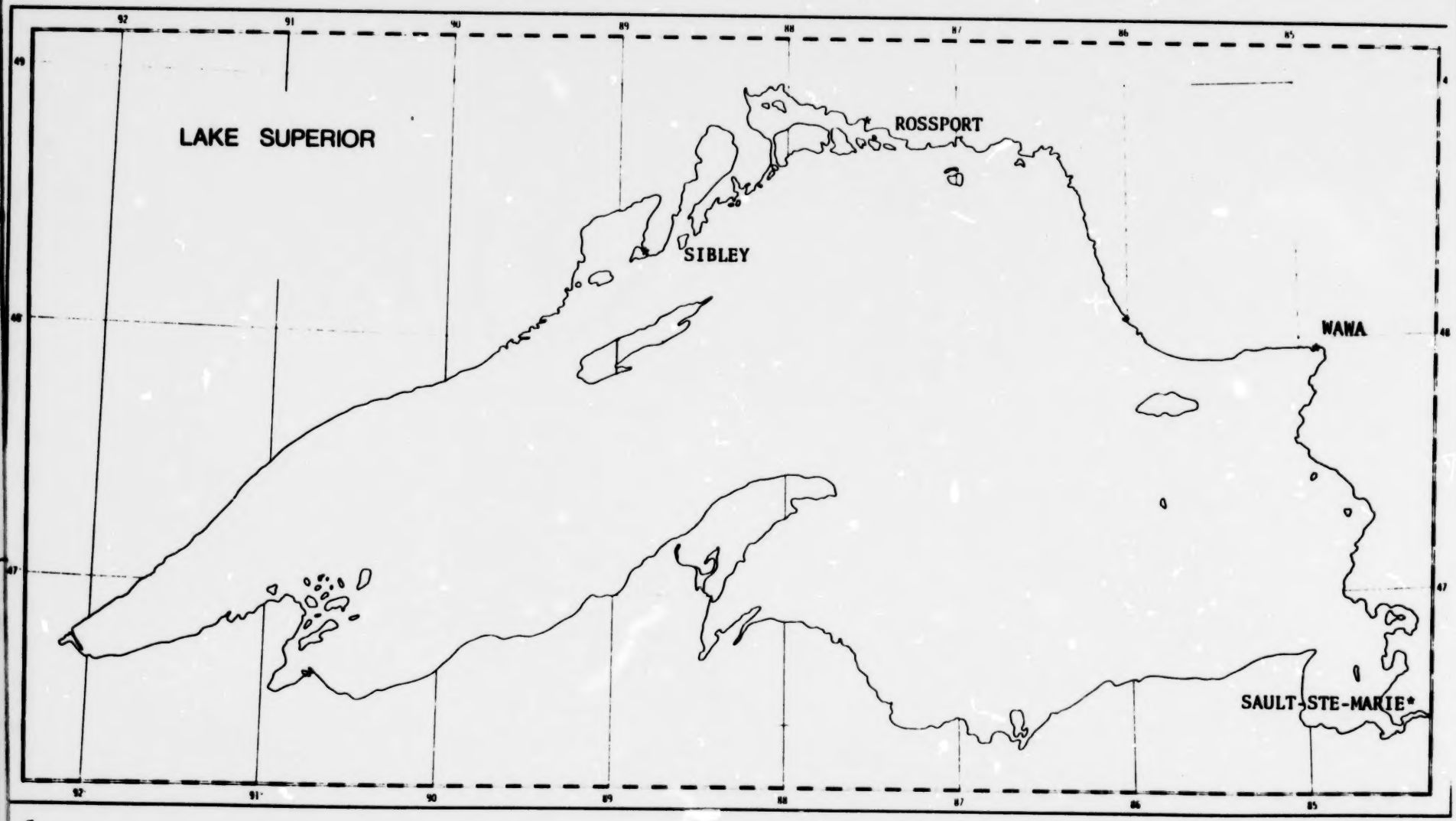

FIG. 1 1983 LAKE SUPERIOR PRECIPITATION SAMPLING STATIONS